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**(19) (CA) APPLICATION FOR CANADIAN PATENT (12)**

(54) **Process and Device for the Reworking of a Dilute Sulphuric Acid Solution Which Contains Dissolved Ferrous Sulphate or a Mixture of Dissolved Metal Sulphates Which Are Mainly Ferrous Sulphate**

(72) **Steinhausen, Helmut - Germany (Federal Republic of) ;**

(73) **Kronos Titan G.m.b.H. - Germany (Federal Republic of) ;**

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ABSTRACT

The invention relates to a process for the reworking of a dilute sulphuric acid solution which contains dissolved ferrous sulphate or a mixture of dissolved metal sulphates which are mainly ferrous sulphate. The sulphuric acid solution is concentrated to a content of up to 40% to 85% by weight  $H_2SO_4$  (% related to the liquid portion), thereby resulting in the formation of a metal sulphate/sulphuric acid slurry. The precipitated metal sulphates are subsequently separated from this slurry.

The purpose of the invention is to enable the separation of the metal sulphates in this process in a technically reliable way using a membrane filter press. The content of free  $H_2SO_4$  in the separated metal sulphates should be on the order of 10% by weight.

As a solution to the problem it is suggested to separate the metal sulphates by pressure filtration in a membrane filter press and to wash the resulting filter cake with a sulphuric acid solution containing 30% to 35% by weight  $H_2SO_4$ . A device suitable therefore is described.

The process is especially suitable for waste acids derived from titanium dioxide production, the sulphuric acid and the metal sulphates being advantageously returnable to the production process.

Process and Device for the Reworking  
of a Dilute Sulphuric Acid Solution Which Contains  
Dissolved Ferrous Sulphate or a Mixture of Dissolved  
Metal Sulphates Which are Mainly Ferrous Sulphate

5       The invention relates to a process for the reworking of a  
dilute sulphuric acid solution which contains dissolved ferrous  
sulphate or a mixture of dissolved metal sulphates consisting  
mainly of ferrous sulphate. The sulphuric acid solution is  
concentrated to from about 40% to about 85% by weight  $H_2SO_4$  (%  
10   related to the liquid portion), thereby resulting in the  
formation of a slurry of metal sulphates and sulphuric acid.  
The precipitate of metal sulphates is subsequently separated  
from this slurry.

15       The invention further relates to a device for carrying out  
such a process.

Numerous variants of the above process have been described  
since some chemical processes produce large amounts of dilute  
sulphuric acid as by-products in which various dissolved metal  
sulphates are present. Formerly these sulphuric acid solutions  
20   used to be considered as a waste product and were dumped in  
public waters. This is no longer done today for reasons of  
environmental protection. Instead, attempts have been made to  
reprocess the sulphuric acid waste solutions in such a way that  
their  $H_2SO_4$  content can be reused in chemical processes. As a  
25   rule, this requires concentrating the dilute sulphuric acid  
solutions to more than about 40% by weight  $H_2SO_4$ . At this  
concentration, most of the metal sulphates dissolved in the  
sulphuric acid precipitate, generally in the form of modifi-  
cations with a low content of water of crystallization. Fer-  
30   rous sulphate for instance crystallizes as monohydrate.

For many uses of the reconcentrated sulphuric acid, these  
precipitated metal sulphates - also known as "filter salt"-  
need to be removed from the acid. In view of the large amounts  
of dilute sulphuric acid reprocessed this way by industry,  
35   methods are looked for whereby only small amounts of the  
valuable, reusable reconcentrated sulphuric acid adhere to the

filter salt after filtration. Moreover, a low content of free sulphuric acid reduces the cost of filter salt disposal since adhering acid would either have to be neutralized before dumping the salt or would, unprofitably, require relatively large amounts of energy if the filter salt were to be thermally decomposed for recovery of  $\text{SO}_2$  and production of sulphuric acid. Separation of the filter salt, however, must be feasible and reliable in a permanent operation.

For these reasons, it is often not feasible to make large-scale use of the above-described processes for reconcentrating dilute sulphuric acid solutions containing metal sulphates. Since many operations (e.g., titanium dioxide production) currently generate enormous quantities of dilute sulphuric acid solution that have to be reprocessed, extended downtimes or interruptions in the reworking process are intolerable without providing expensive storage facilities for the sulphuric acid solutions or throttling the production for the duration of the trouble. In particular, when the dilute sulphuric acid contains large amounts of dissolved ferrous sulphate, the separation of the filter salt from the reconcentrated sulphuric acid still constitutes an unsatisfactorily answered problem.

A known method is to use screen centrifuges for this separation. These centrifuges permit to largely free the filter salt of adhering sulphuric acid. (Forschungsber.-Bundesminist. Forsch. Technol., Technol. Forsch. Entwickl. 1984, BMFT-FB-T-84-150). (Research report by the German Federal Ministry for Research and Technology, 1984, BMFT-FB-T-84-150). However, permanent operation of the centrifuges with the viscous, high-specific-gravity slurry of filter salt/sulphuric acid relatively frequently leads to mechanical damage to the plastic linings of the centrifuge drums at certain spots. As these linings serve to inhibit corrosion and as there is a risk of an unbalanced state, such damages demand immediate repair to prevent more extensive damage to the centrifuges. Repair work on the centrifuge drums normally requires a new balancing of the drums which can be performed only by a few specialized shops,

especially so when the drums are large. Therefore repairs of this type generally take a long time.

It is also possible to use filters for separating the metal sulphates in the slurry from the sulphuric acid. Pressure filtration has been considered in particular because of the high viscosities of the 40% to 85% strength reconcentrated sulphuric acid solutions. EP-A2-133 505 published on February 27, 1985, for instance proposes to concentrate waste acid derived from titanium dioxide production, i.e., a metal sulphate-containing sulphuric acid solution of up to 28% strength, thus obtaining a slurry of metal sulphates and 62% to 70% strength sulphuric acid solution, and to separate the metal sulphates in a chamber filter press. The 62% to 70% strength acid adhering to the filter cake can then be washed out by means of further dilute waste acid or wash acid derived from  $TiO_2$  production (about 8% to 10% strength sulphuric acid). This would reduce the sulphuric acid content of the filter salt to an acceptable level. This procedure, however, implies considerable disadvantages with regard to a trouble-free permanent operation reworking large amounts of sulphuric acid which contains especially ferrous sulphate. The use of a chamber filter press for instance does generally not permit an efficient washing operation since filtration and washing frequently leads to the formation of cracks in the filter cake through which virtually the entire wash solution flows off unutilized. If the filter salt cake contains ferrous sulphate monohydrate, part of the monohydrate is transformed into heptahydrate upon contact with water or dilute waste acid. This transformation leads to a compacting and cementing of the filter cake which is then removed only incompletely and with difficulty from the filter chamber. Owing to the formation of ferrous sulphate heptahydrate, moreover, the filter cloth is often blinded during the washing procedure; in this case filter salt separation has to be interrupted for exchanging or washing the filter cloth. Consequently a largely smooth washing operation cannot be warranted.

EP-A2-194 544 published on September 17, 1986, describes a further process for the concentration of a dilute sulphuric acid solution which contains ferrous sulphate and other metal sulphates. This process does not involve washing of the metal sulphate filter cake. An acceptable level of residual  $H_2SO_4$  in the filter salt is to be achieved by blowing pressurized air through the filter cake as received in filtration at overpressure. The pressurized air blown through the cake is to expel from its capillaries and pores as much adhering reconcentrated acid as possible. If the  $H_2SO_4$  content of the filter salt is to be reduced in this manner by a few percentage points to under 12% by weight, candle filters or leaf filters have to be used which, however, require an expensive periphery in order to function reliably over an extended period of time, as can be taken from EP-A2-235 689, published on September 9, 1987.

Lower  $H_2SO_4$  content of the filter salt cannot be achieved in using a filter press. Even when a membrane filter press is used and when the cake built up during pressure filtration is squeezed at the end of the filtration at high pressure of e.g., 16 bar or 8 bar by aid of the elastic membrane - which is possible with this type of press - the residual  $H_2SO_4$  content of the discharged cake still comes up to 13.2% by weight or 12.3% by weight. In actual practice, however, (e.g., reworking of the waste acid of a  $TiO_2$  plant) a reduction by 1% by weight of the residual  $H_2SO_4$  content in the filter salt can often mean a saving of 500 to 1000 tons sulphuric acid of 100% strength per year. Consequently residual  $H_2SO_4$  contents in the filter salt of more than 12% by weight are considered excessive as a rule. In addition, the high pressures at which the membrane is pressed against the filter cake result in early wear of the membranes, even if specific membrane materials are used. Furthermore, as the filter cake is strongly compacted at pressures above 8 bar, it is rather difficult to blow reconcentrated sulphuric acid out of the capillaries of the cake because the sulphuric acid solution to be expelled from the cake is highly concentrated and therefore very viscous.

The object of the present invention is to avoid the shortcomings of the prior art hereinabove described and to provide a process as mentioned in the beginning which permits to reliably separate the filter salt from the sulphuric acid solution, the separated filter salt having a uniformly low content of free  $H_2SO_4$ .

It has been surprisingly discovered that the reconcentrated sulphuric acid solution, still remaining after filtration, in the cavities of the filter cake consisting of ferrous sulphate monohydrate-containing filter salt, can be washed out without compacting the filter cake or blinding the filter cloth provided the wash liquid is a sulphuric acid solution containing from about 30% to about 35% by weight  $H_2SO_4$ .

The present invention therefore relates to a process for the reworking of a dilute sulphuric acid solution which contains dissolved ferrous sulphate or a mixture of dissolved metal sulphates which are mainly ferrous sulphate. The sulphuric acid solution is concentrated to a content of from about 40% to about 85% by weight  $H_2SO_4$ , (% related to the liquid portion), thereby resulting in the formation of a slurry of metal sulphates and sulphuric acid. The precipitated metal sulphates are subsequently separated from this slurry.

The process is characterized in that:

the separation of the metal sulphates is effected by filtration at overpressure in a membrane filter press, and

the filter cake formed thereby is washed, the wash liquid being a sulphuric acid solution which contains from about 30% to about 35% by weight  $H_2SO_4$ .

The invention further relates to a specific device for carrying out this process.

The washing step using sulphuric acid solution which contains from about 30% to about 35% by weight  $H_2SO_4$ , obviously has the effect of suppressing the dissolution of iron sulphate monohydrate from the filter salt cake and the precipitation of the corresponding heptahydrate from the wash liquid in the

filter cake and filter cloth. Consequently the filter cake is not compacted during washing and the filter cloth is blinded only to the small extent as would be the case if washing non-ferrous metal sulphates. This means that the metal sulphates  
5 can largely be separated from the slurry without difficulty. This considerably facilitates reducing the amount of free sulphuric acid in the filter salt in an industrial-scale operation. It is now possible to separate filter salt  
10 containing large amounts of ferrous sulphate monohydrate by using low-maintenance membrane filter presses instead of centrifuges, at operating conditions which permit a permanent operation without excessive wear, and to reach at the same time residual  $H_2SO_4$  contents in the filter salt of less than 10% by weight.

15 If the reconcentrated sulphuric acid solution adhering to the filter salt is expelled virtually completely by the 30% to 35% strength sulphuric acid wash solution, a residual  $H_2SO_4$  content of 8% by weight or even less can be achieved.

Membrane filter presses as used in the process of the  
20 present invention generally consist of several filter plates, like simple chamber filter presses. In the membrane filter press, however, each of the usual chamber filter plates is doubled by a neighbouring filter plate to which an inflatable membrane is affixed in such a way that the membrane when under  
25 pressure is pressed against the filter cake in the filter chamber to compress the cake uniformly vertically to the cake surface.

These filter presses readily handle slurries with a solids content up to about 50% by weight. Therefore, membrane filter  
30 presses are suitable for all applications of the process of the instant invention in actual practice.

It is a particular advantage of the membrane filter presses that they permit rapid and efficient washing of the filter cake using only small amounts of wash liquid. The  
35 presses are operated in batches, a filtration cycle normally consisting of the following steps:

1) Fill the filter chambers with slurry and allow a filter



cake to build up.

- 2) Squeeze the filter cake.
- 3) Wash the filter cake.
- 4) Press the washed filter cake.
- 5) Blow compressed air through the washed filter cake.
- 6) Discharge the cake from the filter press.

Pressure filtration covers step 1 and optionally step 2. The process of the present invention preferably uses all steps listed above in the order given for separating the precipitated filter salt from the reconcentrated sulphuric acid, but steps 2, 4 and 5 need not all be carried through necessarily.

Compression of the filtered material prior to the washing operation compacts the filter cake and, especially if the latter shows cracks, gaps or similar structural defects, homogenizes it in such a way that the cake throughout its surface has pores of nearly the same size and capillaries with very similar diameters. In the subsequent washing procedure, therefore, the filter cake at all points develops essentially the same resistance to the wash liquid, and the wash liquid therefore does not shortcircuit through larger cracks or channels in the cake in which case the cake would not be washed effectively.

This holds good also for the filter cakes of all subsequent filtrations of slurry batches if the conditions are not changed. Therefore all filter cakes come into contact with virtually the same amount of wash liquid, resulting in a uniformly washed-out filter salt. Moreover, squeezing of the filter cake reduces its moisture content (or increases its solids content). Consequently, lower quantities of 30% to 35% strength sulphuric acid are required in the subsequent washing step to expel the smaller quantity of 40% to 85% strength sulphuric acid solution from the cake. This in turn means a shortened washing operation.

When carrying through the process of the present invention, the pressure must not be too high in squeezing the filter cake before the washing. Excessive pressure would not only

overburden the membranes in the long run, but would compact and drain the filter salt material too much. As a consequence, the filter cake would not be sufficiently permeable for the wash liquid to pass through. No more washing could then be realized. As a rule, the pressure at which the membrane is pressed against the filter cake should range below 8 bar and pressing time should be 5 minutes at most. In many cases, a short squeezing for say 1 minute at a pressure of 5 bar will be sufficient to develop an appropriate structure of the filter salt cake. The optimal pressing conditions naturally are also dependent on the composition of the filtered material, on its mean particle size and on the concentration of the sulphuric acid solution to be expelled; this concentration considerably affects the viscosity of the solution. If necessary, the optimal pressing condition can readily be determined by the expert in two or three scouting experiments.

The wash liquid for washing the filter cake is an aqueous sulphuric acid solution containing 30% to 35% by weight  $H_2SO_4$ . Sulphuric acid solutions with more than 35% by weight  $H_2SO_4$  are also usable in general as they show the same behaviour towards the filter cake in the washing operation as do the 30% to 35% solutions. Their wash-out effect, however, is low, particularly if low-concentration sulphuric acid solutions are washed out of the filter cake.

The wash liquid may contain metal sulphates, e.g. ferrous, aluminum-, magnesium- and other sulphates and in addition, small amounts of chromium sulphate or vanadium sulphate.

There are two different ways of feeding the wash liquid to the filter cake in the press, viz. either through the slurry feed channel of the membrane filter press, i.e., the channel through which the slurry was previously fed to the filter chambers, or through the wash channel. The wash channel (which may also serve other purposes in other steps of the filtration cycle) passes wash liquid only to those filter plates equipped with membranes. The wash liquid is admitted between the possibly inflated - membrane and the filter cake and is dis-

tributed all over the filter cake surface to come out at the opposite side of the filter cake. The wash filtrate is discharged via the filter cloth. Washing by admitting the liquid via the wash channel is preferred because it results in a particularly uniform contact of the filter cake with the wash liquid.

The 40% to 85% strength sulphuric acid solution filling the cavities of the filter cake before the washing operation is slowly expelled from the cake, viz. to the extent that the 30% to 35% strength sulphuric acid wash liquid is forced through the cake. The wash filtrate obtained therefore consists initially of the same 40% to 85% strength sulphuric acid solution as the filtrate obtained in separating the filter salt from the slurry, which separation was performed before the washing. These filtrates should preferably be united.

While the concentrated acid is being expelled, the two sulphuric acid solutions of different concentrations slightly mix with each other at their contact areas so that the concentration of the sulphuric acid in a more or less thick layer drops from the level of the concentrated solution to the level of the wash liquid. Once the sulphuric acid solution of this layer comes out of the filter cake, the sulphuric acid concentration of the filtrate drops relatively rapidly. From a certain moment onward it may therefore often be advisable to stop uniting the filtrate with that recovered initially. This stop is effected preferably when the sulphuric acid concentration of the filtrate has not yet dropped by more than 5% by weight, optimally by less than 1% by weight from its initial level. The desired point can be determined by current - optionally automatic - measurement of the sulphuric acid concentration in the filtrate. In routine cases with unmodified process parameters, one may once measure the period from the moment washing begins till the suitable point is reached and then proceed with the subsequent batches by regularly beginning to separate the wash filtrate from the slurry filtrate after these intervals.

The washed filter cake may additionally be pressed if necessary, and/or compressed air may be blown through it to reduce its moisture content. The cavities of the washed filter cake contain an essentially more dilute sulphuric acid solution than the cake obtained after filtration. And if the filter cake is washed through long enough, it will contain only the wash liquid with 30% to 35% by weight  $H_2SO_4$ .

As the viscosity of sulphuric acid solutions strongly decreases with declining concentration, the more dilute sulphuric acid is much more readily blown out of the washed filter cake by means of compressed air than the relatively concentrated acid adhering to the cake immediately after filtration. This "blowing dry" which serves to expel moisture from the cake, therefore removes more moisture from the washed filter cake and effects a higher solids content than it would if the filter cake had been left as obtained upon filtration. A filter salt with roughly 29% residual moisture (71% solids) is obtained for instance if 5 bar air is blown for 10 minutes through a filter cake separated from a metal sulphate/sulphuric acid slurry with 66.5% by weight  $H_2SO_4$  obtained according to the present invention; and a filter salt with only 22% residual moisture (78% solids) is obtained if the same filter cake is previously washed with a 33% by weight sulphuric acid solution so intensively that the sulphuric acid left in the cake cavities has an average concentration of not more than about 50% by weight  $H_2SO_4$ , and if compressed air is blown through the washed cake under the same conditions as mentioned above. The washed filter cake is blown dry preferably with compressed air of 3 to 6 bar applied for 10 to 15 minutes. The residual content of free  $H_2SO_4$  in the separated metal sulphates should then preferably be at least less than 10% by weight.

In a particularly favourable embodiment of the present invention the dilute sulphuric acid solution is concentrated in several steps, concentration being designed in such a way that in one of the steps the sulphuric acid solution is concentrated up to an  $H_2SO_4$  content of 30% to 35% by weight. Part of this

30% to 35% sulphuric acid solution is branched off and used as wash liquid.

5 In concentrating the dilute sulphuric acid solution, it is advisable to proceed as follows: in a first step evaporate the acid solution to 26% to 29% by weight  $H_2SO_4$  and then cool it down to a temperature of  $10^{\circ}$  to  $25^{\circ}C$ . As a result of the cooling, part of the metal sulphates dissolved in the sulphuric acid precipitate in a form rich in water of crystallization (e.g.,  $FeSO_4 \cdot 7H_2O$ ,  $MgSO_4 \cdot 7H_2O$ ). The high content of crystal-

10 lization water in these metal sulphate modifications effects a further concentration of the 26% to 29% sulphuric acid solution to a content of 30% to 35% by weight  $H_2SO_4$ . After separation of the precipitate from the sulphuric acid solution, the latter is used as wash liquid according to the present invention.

15 In a specific embodiment of the process of this invention, the filtrate obtained at the beginning of the washing treatment is united with the filtrate obtained in the filtration of the metal sulphate/sulphuric acid slurry, for as long as the  $H_2SO_4$  contents of both filtrates do not yet much differ from each other (e.g., by less than 5% by weight). In this procedure,

20 the remainder of the first-mentioned filtrate whose  $H_2SO_4$  content naturally equals at least that of the wash liquid, is returned, preferably wholly, to the concentration step.

25 The process of the present invention is particularly suitable for the reworking of dilute waste acid that is derived from titanium dioxide production by the sulphate route using specifically ilmenite feedstock material. This dilute waste acid is concentrated up to 50% to 75% by weight  $H_2SO_4$ , related to the liquid. In this specific case it is particularly

30 beneficial to combine the process steps as described in the claims.

The resulting reconcentrated sulphuric acid solution can profitably be reused for the digestion of titaniferous feedstock material in the sulphate process. If titanium dioxide

35 pigment of particularly high quality is to be produced in this way from the digested material, the percentage of metal ions

adversely affecting the pigment properties (e.g., chromium and especially vanadium) should be minimized in the digestion mixture. A sufficient amount of the adverse metal ions that originate from contaminations of the titaniferous feedstock are normally discharged in the sulphate process as sulphates via the dilute waste acid and in the subsequent dilute acid reconcentration process via the filter salt. Therefore, care should be taken to ensure that a sufficiently large amount of detrimental metal sulphates is discharged in the overall process and that these sulphates do not accumulate in the recycled sulphuric acid, especially so in continual reconcentration of the dilute waste acid from  $\text{TiO}_2$  pigment production and in recycling of the reconcentrated sulphuric acid obtained in the process of this invention.

If therefore the main part or all of the dilute wash filtrate is returned to the reconcentration stage in the process of this invention, the filter salt must be washed only to the extent that the percentage of detrimental metal sulphates eluted from the filter salt into the wash filtrate is small enough not yet to impair the titanium dioxide hydrate precipitation. If necessary, one has to reduce the quantity of wash liquid or the duration of the washing treatment and tolerate a somewhat higher loss of sulphuric acid not washed out of the filter salt. In turn, a somewhat better capacity of the plant is obtained. It should be noted that the sulphuric acid wash liquid used in the process of this invention and preconcentrated to an  $\text{H}_2\text{SO}_4$  content of 30% to 35% by weight, less tends to elute metal sulphates from the filter cake owing to its higher sulphate concentration than prior art wash liquid or untreated waste acids would do.

The filter salt separated according to this invention is particularly suitable for the recovery of  $\text{SO}_2$  by thermal decomposition due to its low content of free  $\text{H}_2\text{SO}_4$  and residual moisture.

A particularly suitable device for carrying through the process of the present invention comprises:

- a) a first group of structural elements for concentrating the dilute sulphuric acid solution up to an  $H_2SO_4$  content of 30% to 35% by weight;
- 5 b) a second group of structural elements for further concentrating this preconcentrated solution to produce a slurry of metal sulphates and sulphuric acid with an  $H_2SO_4$  content of 40% to 85% by weight, related to the liquid portion;
- c) at least one membrane filter press; and
- 10 d) means to remove the filtered solids and the filtrate from the membrane filter press(es).

In this device, the first group of structural elements has its discharge end connected with the feed end of the second group of structural elements, via conveying means for the 30% to 35% sulphuric acid solution. The discharge end of this 15 latter group is connected, via conveying means for the slurry of metal sulphates/sulphuric acid, with the feed end of the membrane filter press(es).

The device according to the invention is characterized in that it comprises additional conveying means for the 30% to 35% sulphuric acid solution through which the first group of structural elements can bypass the second group of structural elements to discharge directly into the feed end of the slurry feed channel and/or the wash channel of the membrane filter 20 press(es), and that the discharge end(s) of the membrane filter press(es) can be connected with the feed end of the second group of structural elements through additional conveying means for returning the filtrate. This device provides, in a particularly simple way, suitable wash liquid for the washing procedure according to this invention. When the  $H_2SO_4$  content of the wash filtrate discharged from the membrane filter press drops 25 to an inacceptably low value during or after the washing procedure, this filtrate whose  $H_2SO_4$  content is naturally higher than 30% to 35%, may be passed to the second concentration stage to replace previously withdrawn wash liquid. 30

The two groups of structural elements for the concen- 35

tration section of the device may be made up in any way appearing appropriate to one skilled in the art.

5 The first structural group for instance may consist of one or several scrub towers (e.g., venturi scrubbers) in which the initial solution is preconcentrated by means of hot exhaust gases. In many cases it is appropriate to install a cooling crystallization unit upstream of the scrubber and a filter to separate metal sulphates rich in water of crystallization, especially  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , since their separation enables an inexpensive further concentration of the sulphuric acid solution to the desired  $\text{H}_2\text{SO}_4$  content of 30% to 35% by weight. Another specific design of the first structural group can be taken from Canadian Patent Application No. 581,141 of the Applicant, whose disclosure is hereby referred to.

15 The second structural group in which the preconcentrated 30% to 35% sulphuric acid solution is further concentrated thereby forming a slurry of metal sulphates and sulphuric acid solution with an  $\text{H}_2\text{SO}_4$  content of 40% to 85% by weight, may consist for instance of a multi-stage vacuum circulation evaporator. The evaporator may be followed by a cooler or heat exchanger to recover waste heat, and/or by an agitated-vessel cascade in which the precipitated metal sulphate crystals may "mature" to adjust the particle size range best suited for separation in the membrane filter press.

25 "Conveying means" are understood to be any means that one skilled in the art considers suitable for conveying sulphuric acid solutions or slurries of the defined  $\text{H}_2\text{SO}_4$  contents between the parts of the devices mentioned. These means comprise for example piping and pumps.

30 If necessary, a device has to be provided additionally for removing sulphuric acid fumes from the exhaust air resulting from dry-blowing the filter cake in the membrane filter press.

The invention is illustrated by, but not limited by, the following Examples.

35

#### EXAMPLE 1

A waste acid as obtained in the production of titanium



dioxide by the sulphate route using ilmenite feedstock, was reprocessed by the process of this invention. The waste acid had the following composition:

	<u>Constituents</u>	<u>% by weight</u>
5	FeSO <sub>4</sub>	11.00
	MgSO <sub>4</sub>	2.33
	TiOSO <sub>4</sub>	0.87
	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.25
	MnSO <sub>4</sub>	0.19
10	VO SO <sub>4</sub>	0.13
	CaSO <sub>4</sub>	0.10
	Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.08
	H <sub>2</sub> SO <sub>4</sub>	22.90
	H <sub>2</sub> O/trace elements	balance

15 The slurry of sulphuric acid solution and precipitated metal sulphates had an H<sub>2</sub>SO<sub>4</sub> content of 66.5% by weight, related to the liquid. the particle diameter of the salts essentially ranged between 10 and 30 microns (determined under the microscope).

20 a) (Comparison) 5 Kg of the slurry of roughly 50°C were filtered in a membrane filter press consisting of one chamber and having a filter area of 200 x 220 mm, the slurry being fed to the filter chamber at a pressure of 5 bar. After 30 seconds, the filter cake was compressed for  
25 roughly one minute at a pressure of 5 bar. Cake thickness was 20 mm, residual moisture 40.7% by weight (corresponding to only 59.3% by weight solids). The filter cake contained 27.1% free H<sub>2</sub>SO<sub>4</sub>.

b) (Comparison) Procedure as described under a). After compression, however, 5 bar air was blown for 10 minutes  
30 through the filter cake. The residual moisture of the cake was 28.9% by weight (71.1% by weight solids). The H<sub>2</sub>SO<sub>4</sub> content in the cake was analyzed to amount to 19.6%.

Owing to the different partial vapour pressures of water and  $\text{H}_2\text{SO}_4$ , the  $\text{H}_2\text{SO}_4$  concentration in the sulphuric acid solution adhering to the cake had risen to 67.8% by weight after through-blowing.

- 5 c) Procedure as under a). After filtration, however, the filter cake was washed with 0.25 litres of dilute waste acid preconcentrated to 33% by weight  $\text{H}_2\text{SO}_4$  of  $20^\circ\text{C}$ . Subsequently, 5 bar air was again blown through the cake for 10 minutes. Residual moisture of the cake was 24.6% by weight (75.4% by weight solids). Residual  $\text{H}_2\text{SO}_4$  content was 14.6% by weight.
- 10 d) Procedure was equal to that described under c). However, 0.5 litre of the 33% sulphuric acid solution was used for washing the filter cake. Residual moisture of the cake was 23.3% by weight (76.7% by weight solids). The analysis of the  $\text{H}_2\text{SO}_4$  content in the cake showed 13.2% by weight.
- 15 e) The experimental parameters were the same as in c) above. The filter cake, however, was washed with 1.5 litres of the same wash liquid. The residual cake moisture was 21.9% by weight (78.1% by weight solids) at 10% weight  $\text{H}_2\text{SO}_4$  content. This corresponds to an  $\text{H}_2\text{SO}_4$  concentration in the sulphuric acid solution in the cake of 45.7% by weight.
- 20

25

#### EXAMPLE 2

The same procedure was used as described in Example 1. The slurry obtained in concentrating the waste acid, however, was allowed to mature for a short while before the metal sulphates were separated. Hence, their particle size was slightly larger than in Example 1.

30

- a) (Comparison) The experimental parameters equalled those of Example 1b). The residual moisture of the filter salt was only 23.5% by weight (76.5% by weight solids). The analysis of free  $\text{H}_2\text{SO}_4$  showed a residual content of 15.6% by weight (corresponding to 66.6% by weight  $\text{H}_2\text{SO}_4$  concentration in the sulphuric acid adhering to the filter salt).
- 35

- b) Experimental conditions were the same as in a) above. But the cake was washed with 1 litre of waste acid preconcentrated to 33% by weight  $H_2SO_4$ . The filter salt cake then contained 19.6% by weight residual moisture and 8.8% by weight  $H_2SO_4$ .

#### EXAMPLE 3

In this Example the particle size of the metal sulphates to be separated from the slurry essentially ranged between 15 and 70 microns. The  $H_2SO_4$  content of the slurry was 65.2% by weight related to liquid.

- a) (Comparison) The other experimental conditions were the same as in Example 1b). The separated metal sulphates had a residual moisture content of 19.8% by weight. The content of adhering free  $H_2SO_4$  was 13% by weight. The  $H_2SO_4$  concentration in the adhering acid was therefore 65.7% by weight.
- b) In modifying Experiment a), the filter cake was first washed with 0.75 litre of the waste acid preconcentrated to 33% by weight. The residual moisture in the cake was 17% by weight with an  $H_2SO_4$  content of 8.3% by weight.
- c) Washing with 1 litre preconcentrated acid, with the other parameters remaining the same as in b) above, resulted in a filter salt with 17% residual moisture and 8.0% by weight free  $H_2SO_4$ .

#### EXAMPLE 4

In an experiment close to actual production practice, waste acid containing ferrous sulphate and obtained in the titanium dioxide production from ilmenite feedstock, was first preconcentrated in several steps to 32% to 33% by weight  $H_2SO_4$ . Solids were then separated from the acid. A small part of this preconcentrated waste acid was used as wash liquid. The majority was further concentrated until the  $H_2SO_4$  content of the resulting slurry of sulphuric acid solution and metal sulphates (chiefly ferrous sulphate monohydrate) was 68% to 70% by weight, related to liquid.

These metal sulphates were separated from the slurry using

a membrane filter press. The filter press had two chambers, each 50 mm deep, and a total filter area of 4.5 m<sup>2</sup>. The membranes were made of rubber.

5 The Table on pages 19 and 20 gives a survey of these experiments. In Experiments 4a to 4f the filter salt cake was washed according to the present invention. In Experiments 4a to 4c wash liquid was fed via the slurry channel and also via the wash liquid channel whereas in Experiments 4d to 4f the wash liquid was fed only via the wash liquid channel. In  
10 Experiments 4g to 4i the filter salt was not washed for comparison.

None of the experiments using filter salt washing showed a compaction of the cake or blinding of the filter cloth as a result of washing.

15 Line #15 of the Table shows that the H<sub>2</sub>SO<sub>4</sub> content of the filter salt cake could readily be reduced by more than 50%. The vanadium content of the filter salt could be kept at the same level as would be obtained without filter salt washing (cf. especially Experiments 4d to 4i, line #17). Hence, the  
20 adverse metal ions need not be suspected to markedly accumulate in the reconcentrated sulphuric acid as a result of returning the wash filtrate to the concentration stage.

If not otherwise stated, "%" in this text and table means percent by weight (% by weight).

TABLE

Slurry used	a	b	c	d	e	f	g	h	i
1. H <sub>2</sub> SO <sub>4</sub> (% by weight)	69.0	69.7	68.4	69.5	69.5	69.3	69.5	69.5	69.5
2. Solids (% by weight)	26.0	26.0	26.3	27.1	27.1	27.2	27.9	27.9	27.9
<u>Filtration</u>									
3. Filtration time (min)	3.5	3.0	4.0	1.5	2.0	2.0	3.0	1.5	1.3
Filtration pressure (bar)	2.5	2.2	2.4	2.0	2.4	2.4	2.0	2.0	2.0
4. Compression time (min)	3.0	2.0	3.0	1.5	2.0	3.0	-	-	-
Pressure (bar)	4.0	4.0	4.0	4.0	4.0	4.0	-	-	-
<u>Washing</u>									
analytical data of wash acid solution									
5. H <sub>2</sub> SO <sub>4</sub> (% by weight)	32.8	33.0	33.1	32.6	32.6	32.1			
6. Fe	3.3	3.2	3.4	2.5	2.5	3.1			
7. Al	0.064	0.069	0.069	0.069	0.069	0.070			
8. Cr	0.031	0.033	0.034	0.044	0.044	0.034			
9. V	0.066	0.074	0.074	0.076	0.076	0.075			
10. Washing time (min)	15.0	8.0	9.0	4.0	4.5	4.0			
Washing pressure (bar)	2.0-3.2	2.2-3.2	2.4-3.5	3.2	3.2	3.4			
11. Wash liquid used (kg)	109.0	91.0	77.0	39.0	38.0	25.0			

no washing

TABLE Continued

	a	b	c	d	e	f	g	h	i
<u>Post-pressing</u>									
12. Time (minutes)	5.0	3.0	3.0	3.0	3.5	3.0	3.0	2.5	2.7
Pressure (bar)	6.0	6.0	6.0	6.0	7.0	7.0	8.0	8.0	8.0
<u>Dry-blowing</u>									
13. Time (minutes)	10.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0
Pressure (bar)	4.0	4.0	5.0	5.0-4.5	4.0	4.0	6.0	6.0	6.0
<u>Products</u>									
<u>Filter salt</u>									
14. Cake thickness (mm)	35.0	38.0	41.0	26.0	28.0	29.0	37.0	32.0	29.0
Cake weight (kg)	126.0	140.0	149.0	92.0	101.0	104.0	134.0	115.0	105.0
15. H <sub>2</sub> SO <sub>4</sub> (% by weight)	9.4	10.2	9.4	9.5	9.3	10.4	23.3	23.6	23.0
16. Residual moisture (wt %)	24.2	23.9	23.2	21.5	21.3	21.6	32.3	32.5	31.6
Solids (% by weight)	75.8	76.1	76.8	78.5	78.7	78.4	67.7	67.5	68.4
17. V (% by weight)	0.17	0.21	0.23	0.29	0.28	0.31	0.25	0.27	0.26
<u>Reconcentrated sulphuric acid solution</u>									
18. H <sub>2</sub> SO <sub>4</sub> (% by weight)	69.3	68.5	68.5	68.8	68.8	68.1	68.9	68.9	68.9
19. V (% by weight)	0.028	0.033	0.038	0.027	0.027	0.035	0.034	0.034	0.034

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for the reworking of a dilute sulphuric acid solution which contains dissolved ferrous sulphate or a mixture of dissolved metal sulphates consisting mainly of ferrous sulphate, the sulphuric acid solution being concentrated to a content of from about 40% to about 85% by weight  $H_2SO_4$  (said % related to the liquid portion), thereby resulting in the formation of a metal sulphate/sulphuric acid slurry and the precipitated metal sulphates being subsequently separated from the slurry, which comprises effecting the separation of the metal sulphates by filtration at overpressure in a membrane filter press and washing the filter cake thus formed, the wash liquid being a sulphuric acid solution which contains from about 30% to about 35% by weight  $H_2SO_4$ .

2. The process of claim 1 wherein the filtration consists of a first step in which the filter cake builds up, and a second step in which the filter cake is squeezed.

3. The process of claim 1 wherein compressed air is blown through the washed filter cake.

4. The process of claim 2 wherein, after squeezing, compressed air is blown through the washed filter cake.

5. The process of claim 2 or 4 wherein squeezing is effected at a pressure up to a maximum of about 8 bar.

6. The process of claim 3 or 4 wherein compressed air of from about 3 to about 6 bar is blown through the filter cake for from about 10 to about 15 minutes.

7. The process of claim 1, 2 or 3 wherein the residual content of free  $H_2SO_4$  in the separated metal sulphates is less

than about 10% by weight.

8. The process of claim 1, 2 or 3 wherein the wash liquid of from about 30% to about 35% by weight  $H_2SO_4$  contains dissolved metal sulphates.

9. The process of claim 1, 2 or 3 wherein the wash liquid of from about 30% to about 35% by weight  $H_2SO_4$  contains dissolved ferrous sulphate.

10. The process of claim 1, 2 or 3 wherein the wash liquid of from about 30% to about 35% by weight  $H_2SO_4$  contains dissolved metal sulphates and wherein the concentration of dilute sulphuric acid solution to from about 40% to about 85% by weight  $H_2SO_4$  (said % relates to the liquid portion) is effected in several steps, the solution being concentrated to from about 30% to about 35% by weight  $H_2SO_4$  in one of the steps and part of this solution being used as the wash liquid.

11. The process of claim 1, 2 or 3 wherein the wash liquid of from about 30% to about 35% by weight  $H_2SO_4$  contains dissolved ferrous sulphate and wherein the concentration of dilute sulphuric acid solution to from about 40% to about 85% by weight  $H_2SO_4$  (said % related to the liquid portion) is effected in several steps, the solution being concentrated to from about 30% to about 35% by weight  $H_2SO_4$  in one of the steps and part of this solution being used as the wash liquid.

12. The process of claim 1, 2 or 3 wherein the wash liquid of from about 30% to about 35% by weight  $H_2SO_4$  contains dissolved metal sulphates and wherein the concentration of dilute sulphuric acid solution to from about 40% to about 85% by weight  $H_2SO_4$  (said % related to the liquid portion) is effected in several steps and wherein said dilute sulphuric acid solution in a first step is concentrated by evaporation to a content of from about 26% to about 29% by weight  $H_2SO_4$ , subse-



quently cooled to a temperature of from about  $10^{\circ}$  to about  $25^{\circ}\text{C}$  and freed from the precipitated metal sulphates rich in water of crystallization, especially  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , and this free sulphuric acid solution now having a strength of from about 30% to about 35% by weight  $\text{H}_2\text{SO}_4$  is used as the wash liquid.

13. The process of claim 1, 2 or 3 wherein the wash liquid of from about 30% to about 35% by weight  $\text{H}_2\text{SO}_4$  contains dissolved ferrous sulphate and wherein the concentration of dilute sulphuric acid solution to from about 40% to about 85% by weight  $\text{H}_2\text{SO}_4$  (said % related to the liquid portion) is effected in several steps and wherein said dilute sulphuric acid solution in a first step is concentrated by evaporation to a content of from about 26% to about 29% by weight  $\text{H}_2\text{SO}_4$ , subsequently cooled to a temperature of from about  $10^{\circ}$  to about  $25^{\circ}\text{C}$  and freed from the precipitated metal sulphates rich in water of crystallization, especially  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , and this free sulphuric acid solution now having a strength of from about 30% to about 35% by weight  $\text{H}_2\text{SO}_4$  is used as the wash liquid.

14. The process of claim 1, 2 or 3 wherein the filtrate obtained from the beginning of the washing is initially united with the filtrate obtained during the filtration, and at least part of the residual wash filtrate is returned to the concentration stage.

15. The process of claim 1, 2 or 3 wherein the filtrate obtained from the beginning of the washing is united with the filtrate obtained during the filtration until its  $\text{H}_2\text{SO}_4$  content is not more than 5% by weight lower than the  $\text{H}_2\text{SO}_4$  content of the filtrate derived from said filtration, and the residual wash filtrate is returned to the concentration stage.

16. The process of claim 1, 2 or 3 wherein the dilute sulphuric acid solution treated in said process is waste acid derived from titanium dioxide production and said waste acid is

concentrated to from about 50% to about 75% by weight  $H_2SO_4$  (said % related to the liquid portion).

17. The use of a concentrated sulphuric acid solution, prepared by the process of claim 1, 2 or 3, in the digestion of titaniferous feedstock material.

18. The use of filter cake containing metal sulphates, prepared by the process of claim 1, 2 or 3, for the recovery of  $SO_2$  by thermal decomposition.

19. The process of claim 4 wherein the residual content of free  $H_2SO_4$  in the separated metal sulphates is less than about 10% by weight.

20. The process of claim 4 wherein the wash liquid of from about 30% to about 35% by weight  $H_2SO_4$  contains dissolved metal sulphates.

21. The process of claim 4 wherein the wash liquid of from about 30% to about 35% by weight  $H_2SO_4$  contains dissolved ferrous sulphate.

22. The process of claim 4 wherein the wash liquid of from about 30% to about 35% by weight  $H_2SO_4$  contains dissolved metal sulphates and wherein the concentration of dilute sulphuric acid solution to from about 40% to about 85% by weight  $H_2SO_4$  (said % relates to the liquid portion) is effected in several steps, the solution being concentrated to from about 30% to about 35% by weight  $H_2SO_4$  in one of the steps and part of this solution being used as the wash liquid.

23. The process of claim 4 wherein the wash liquid of from about 30% to about 35% by weight  $H_2SO_4$  contains dissolved ferrous sulphate and wherein the concentration of dilute sulphuric acid solution to from about 40% to about 85% by weight

H<sub>2</sub>SO<sub>4</sub> (said % related to the liquid portion) is effected in several steps, the solution being concentrated to from about 30% to about 35% by weight H<sub>2</sub>SO<sub>4</sub> in one of the steps and part of this solution being used as the wash liquid.

24. The process of claim 4 wherein the wash liquid of from about 30% to about 35% by weight H<sub>2</sub>SO<sub>4</sub> contains dissolved metal sulphates and wherein the concentration of dilute sulphuric acid solution to from about 40% to about 85% by weight H<sub>2</sub>SO<sub>4</sub> (said % related to the liquid portion) is effected in several steps and wherein said dilute sulphuric acid solution in a first step is concentrated by evaporation to a content of from about 26% to about 29% by weight H<sub>2</sub>SO<sub>4</sub>, subsequently cooled to a temperature of from about 10° to about 25°C and freed from the precipitated metal sulphates rich in water of crystallization, especially FeSO<sub>4</sub>.7H<sub>2</sub>O, and this free sulphuric acid solution now having a strength of from about 30% to about 35% by weight H<sub>2</sub>SO<sub>4</sub> is used as the wash liquid.

25. The process of claim 4 wherein the wash liquid of from about 30% to about 35% by weight H<sub>2</sub>SO<sub>4</sub> contains dissolved ferrous sulphate and wherein the concentration of dilute sulphuric acid solution to from about 40% to about 85% by weight H<sub>2</sub>SO<sub>4</sub> (said % related to the liquid portion) is effected in several steps and wherein said dilute sulphuric acid solution in a first step is concentrated by evaporation to a content of from about 26% to about 29% by weight H<sub>2</sub>SO<sub>4</sub>, subsequently cooled to a temperature of from about 10° to about 25°C and freed from the precipitated metal sulphates rich in water of crystallization, especially FeSO<sub>4</sub>.7H<sub>2</sub>O, and this free sulphuric acid solution now having a strength of from about 30% to about 35% by weight H<sub>2</sub>SO<sub>4</sub> is used as the wash liquid.

26. The process of claim 4 wherein the filtrate obtained from the beginning of the washing is initially united with the filtrate obtained during the filtration, and at least part of

the residual wash filtrate is returned to the concentration stage.

27. The process of claim 4 wherein the filtrate obtained from the beginning of the washing is united with the filtrate obtained during the filtration until its  $H_2SO_4$  content is not more than 5% by weight lower than the  $H_2SO_4$  content of the filtrate derived from said filtration, and the residual wash filtrate is returned to the concentration stage.

28. The process of claim 4 wherein the dilute sulphuric acid solution treated in said process is waste acid derived from titanium dioxide production and said waste acid is concentrated to from about 50% to about 75% by weight  $H_2SO_4$  (said % related to the liquid portion).

29. The use of a concentrated sulphuric acid solution, prepared by the process of claim 4, in the digestion of titaniferous feedstock material.

30. The use of filter cake containing metal sulphates, prepared by the process of claim 4, for the recovery of  $SO_2$  by thermal decomposition.

31. A device for the reworking of a dilute sulphuric acid solution which contains dissolved ferrous sulphate or a mixture of dissolved metal sulphates consisting mainly of ferrous sulphate, the device containing:

- a) a first group of structural elements for the preconcentration of the dilute sulphuric acid solution up to an  $H_2SO_4$  content of from about 30% to about 35% by weight;
- b) a second group of structural elements for the further concentration of this preconcentrated solution to produce a slurry of metal sulphates and sulphuric acid with an  $H_2SO_4$  content of from about 40% to about 85% by weight (said % related to the liquid portion);

- c) at least one membrane filter press; and
- d) means to remove filtered solids and filtrate from said membrane filter press(es);

said first group of structural elements having its discharge end connected, via conveying means for the from about 30% to about 35% sulphuric acid solution, with the feed end of said second group of structural elements and said second group having its discharge end connected with the feed end(s) of said membrane filter press(es) via conveying means for said metal sulphate/sulphuric acid slurry, the device being characterized in that it additionally comprises conveying means for the from about 30% to about 35% sulphuric acid solution through which said first group of structural elements can bypass said second group of structural elements to discharge directly into the feed end of the slurry feed channel and/or the wash channel of said membrane filter press(es) and that the discharge end(s) of said membrane filter press(es) can be connected with the feed end of said second group of structural elements, via conveying means, for returning filtrate.

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